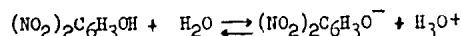


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If we consider these transformations and their effect on activity of the aromatic nucleus toward nitrating agents, then it is not surprising that the rate of nitration of aromatic acids in anhydrous sulfuric acid increases 10-20 times after addition of small quantities of water. The nitration rates of aromatic substances, reacting only with acids but lacking ionogenic hydrogen, such as nitrocompounds, are increased only three times in this case. (2) Further additions of water sharply lower the concentration of the active nitrating agent, the nitronium cation, and, therefore, cause a decrease in the reaction rate.

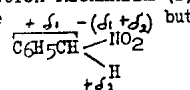
The ideas developed, along with several theoretical considerations, led us to the conclusion that aromatic substances which have an acidic nature in sufficiently diluted nitric acid enter the nitration reaction exclusively in the form of anions. This condition was proved experimentally for the nitration of nitrophenols. It was first shown that nitrophenols are nitrated with dilute nitric acid through an intermediate reaction with nitrogen dioxide. It was further found that they react very slowly with nitrogen dioxide when lacking a possibility for electrolytic dissociation, for example, in only polar carbon tetrachloride ($\epsilon = 2.2$), in which o-nitrophenol typically forms an almost colorless solution. The action of nitrogen dioxide on colored solutions of nitrophenol in polar nitromethane ($\epsilon = 39.4$) led to rapid nitration on heating. Finally, the reaction between nitrogen dioxide and nitrophenolates of alkali metals which definitely have an ionic structure took place practically instantaneously. All of these experiments force us to acknowledge the fact that nitration in dilute acid takes place through the interaction of nitrogen dioxide and nitrophenol anions by the scheme:



We believe that nitration of the H_2O_4 anion takes place according to the mechanism presented in our previous report. (4)

Clarification of the role of ionization allowed us to understand the paradox of the change in the rate of nitration of the paraffinic chain with nitric acid in the presence of nitrogen dioxide in the series $\text{C}_6\text{H}_5\text{CH}_3$, $\text{C}_6\text{H}_5\text{CH}_2\text{NO}_2$, $\text{C}_6\text{H}_5\text{CH}(\text{NO}_2)_2$: in the transition from toluene to phenylnitromethane, the reaction rate decreased sharply, almost to zero, but, after introduction of the second nitro group, it sharply increased. The principal reaction product in the latter case turned out to be the previously unknown phenyltrinitromethane.

The nitration rate of the side chain of toluene is determined by the reaction (5) $\text{C}_6\text{H}_5\text{CH}_2 - \text{H} + \text{NO}_2 \rightarrow \text{C}_6\text{H}_5\text{CH}_2 + \text{HNO}_2$. In brief, the velocity of this reaction depends on the stability of the formed radical and the nucleophilic character of the detached hydrogen. The nucleophilic character of hydrogen will be lowered when a nitro group is introduced, which agrees with our observation of the great decrease of the nitration rate with NO_2 in the transition from toluene to ar-nitrotoluene under preservation of the type of reaction mechanism (1). This circumstance explains the inertness of phenylnitromethane

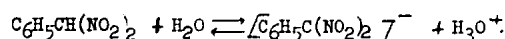


the activity of phenyldinitromethane detected by us, should, it seems, be in direct contradiction with this influence of the nitro group and with the known rules of nitration of dinitro derivatives in the nucleus.

The contradiction is explained if it is taken into account that the phenyldinitromethane, possessing an acidic character, dissociates to some extent in dilute nitric acid and enters the reaction with NO_2 in the form of a more nucleophilic anion. The explanation now advanced is based on a series of experiments.

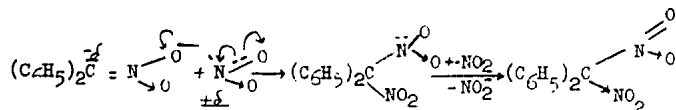
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Thus, it was found that phenyldinitromethane dissolves in carbon tetrachloride without the color which is typical for its anion, and in conformity with this, does not react with nitrogen dioxide in this solvent, whereas the reaction proceeds noticeably in nitromethane and very rapidly in colored pyridine solutions, in which, undoubtedly, there takes place a significant formation of the anion: $C_6H_5CH(NO_2)_2 + C_6H_5N \rightleftharpoons [C_6H_5C(NO_2)_2]^- + [C_6H_5NH]^+$. The reaction between nitrogen dioxide and potassium phenyldinitromethane $[C_6H_5C(NO_2)_2]^-K^+$ took place practically instantaneously on addition of nitrogen dioxide to an alkaline solution of phenyldinitromethane; in this case, the nitration rate was of the same order as the hydrolysis rate of nitrogen dioxide. All of these observations confirm the plausibility of our interpretations to the effect that the nitration of phenyldinitromethane by nitrogen dioxide in an acid-water medium passes through an ionization stage:



The fact that this process takes place is proved by the coloration of water and alcohol solutions of phenyldinitromethane.

The nitration mechanism of this type of anions is explained by studying the reaction of nitrogen dioxide with potassium diphenylnitromethane $[(C_6H_5)_2CNO_2]^-K^+$. It developed that the reaction gives an almost 100% yield of the dinitro compound $(C_6H_5)_2C(NO_2)_2$ at 100° C and runs especially smoothly at 0° C, giving the same yield. This forces one to discard the notion of an intermediate formation of the $(C_6H_5)_2CNO_2$ radical and to assume that in the primary reaction taking place here, there is addition of NO_2 to the coordinatively unsaturated carbon.



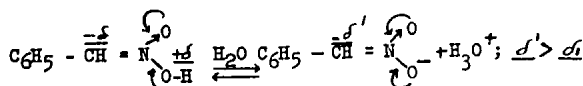
The formed radical anion, giving up its spare electron to the second molecule of NO_2 , becomes a dinitro compound. According to the nature of its first stage, this reaction must be regarded as an ion-complex process.

From the above, it follows that the extreme members of $C_6H_5CH_3$, $C_6H_5CH_2NO_2$, and $C_6H_5CH(NO_2)_2$ are nitrated by NO_2 in the paraffinic chain by different mechanisms. Neither of the two ways is readily open to the middle member, and, therefore, there is practically no reaction between phenylnitromethane and nitric acid in the presence of NO_2 .

In a solution of phenyldinitromethane in nitric acid of 1.5 spgr or a strong nitrating mixture, formation of the anion $[C_6H_5C(NO_2)_2]^-$ is highly improbable. The nitronium cation $[NO_2]^+$ arising under these conditions reacts with an undissociated molecule of the nitrocompound in the aromatic ring to form meta-nitrophenyldinitromethane. Nitration of phenyltrinitromethane with a nitric and sulfuric acid mixture results in the previously unknown meta-nitrophenyltrinitromethane, 65°C mp.

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We also discovered that the aci- form of phenylnitromethane enters into reaction with nitrogen dioxide comparatively easily. The activity of the former is explained, as before, by a combination of coordinative unsaturation at the alpha carbon and increased nucleophilicity, as well as transition into a more reactive anion:



We shall describe some of the experiments on the nitration of phenyldinitromethane.

1. Nitration of Potassium Phenyldinitromethane

Nine grams of potassium salt of the dinitro compound with 20 ml of CCl_4 . To this mixture, at -12°C , 6 ml of nitrogen dioxide in 10 ml of CCl_4 were added with stirring. After treating the reaction mixture with water, a solution of soda, and removing the solvent under vacuum, about 7 g of crude phenyltrinitromethane were obtained. For purification, the product was treated with 5 ml of concentrated H_2SO_4 . After freezing the separated upper layer and filtering the crystals with suction, pure phenyltrinitromethane with $+4.5^\circ\text{C}$ mp was obtained.

$$\begin{array}{l} \text{Found \%: N 18.81, 1870; MW} = 225 \\ \text{C}_7\text{H}_5\text{O}_6\text{N}_3\% \text{ Calculated: N 18.5} \quad \text{MW} = 227 \\ d_4^{20} = 1.4002, n_D^{20} = 1.5375. \text{MRD} = 50.52 \end{array}$$

In conformity with the assumed constitution, the product yielded benzoic acid when heated with concentrated H_2SO_4 and the potassium salt of phenyldinitromethane when heated with alcoholic KOH.

Phenyltrinitromethane decomposes rather quickly, even at room temperature. It is remarkable that when this happens (or still later after standing in nitric acid with nitrogen dioxide) this substance is transformed into para-nitrobenzoic acid. By introducing 5 g of the product to a mixture of 3 ml of HNO_3 (sp gr 1.52) and 6 ml of 20% oleum at a temperature of 40.45°C , it turns into crystalline meta-nitrophenyltrinitromethane. After a twofold recrystallization of the crude product obtained from methanol, it melted at 65°C .

$$\begin{array}{l} \text{Found \%: N 20.49} \\ \text{CH}_4\text{O}_8\text{N}_4 \text{ Calculated \%: N 20.58} \end{array}$$

In conformity with the assumed constitution, the product yielded meta-nitrobenzoic acid when heated with concentrated H_2SO_4 and meta-nitrophenyldinitromethane, $122-123^\circ\text{C}$ mp, when heated with alcoholic KOH.

2. Reaction of Phenyldinitromethane With NO_2 in Organic Solvent

The reaction did not proceed noticeably in CCl_4 after many days of standing, not after 3 hr of heating 100°C in a sealed tube; in a solution of nitromethane under the latter conditions, about 20% of the phenyldinitromethane reacted. To learn the effect of pyridine, the following experiment was carried out. Two grams of phenyldinitromethane were dissolved in 2 ml of base, and the resulting solution was quickly added under stirring to 6 ml of nitrogen dioxide in 20 ml of CCl_4 . By means of the previously described treatment, 1.1 g of crude phenyltrinitromethane were obtained; about 0.7 g of phenyldinitromethane was recovered from the soda extract.

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3. Nitration of Phenyldinitromethane With Nitric Acid

A mixture of one gram of phenyldinitromethane and 10 ml of nitric acid of 1.4 spgr containing oxides of nitrogen, was left standing for 10 days. After dilution with water and addition of CCl_4 , 0.32 g of para-nitrobenzoic acid was filtered off. This is the conversion product of a part of the phenyltrinitromethane that is formed under these conditions. A total of 0.60 g of phenyltrinitromethane was obtained from the CCl_4 extract after distilling the solvent.

With no oxides of nitrogen present, no reaction was observed even after standing for 2 months.

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